

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 12/00/75		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE TREATABILITY STUDIES OF SEEP WATER FROM THE BOG AT ROCKY MOUNTAIN ARSENAL				5. FUNDING NUMBERS	
6. AUTHOR(S) CARNAHAN, R.; LENT, D.; ANZZOLIN, R.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT CENTER FORT BELVOIR, VA				8. PERFORMING ORGANIZATION REPORT NUMBER 81339R25	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) ROCKY MOUNTAIN ARSENAL (CO.) COMMERCE CITY, CO				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) THIS REPORT COVERS LABORATORY INVESTIGATIONS OF PROCEDURES, DISCUSSION OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS FOR SEVERAL WATER TREATMENT PROCESSES UTILIZING CARBON ADSORPTION, REVERSE OSMOSIS, AND CHEMICAL OXIDATION FOR DECONTAMINATION WASTEWATER. THE FIRST PHASE OF THE STUDY CONCERNS THE REMOVAL OR DESTRUCTION OF TRACE ORGANICS IN THE SEEP WATER. THE SECOND PHASE INVOLVES SELECTING THE MOST FEASIBLE PROCESSES FOR SCALE-UP. CONCLUSIONS: (1) REVERSE OSMOSIS IS A FEASIBLE PROCESS FOR TREATING THE SEEP WATER, (2) POWDER CARBON/COAGULATION IS THE MOST PRACTICAL METHOD OF TREATING THE WASTE, SINCE IT PROVIDES FLEXIBILITY AND CONTROL, (3) GRANULAR CARBON ADSORPTION, AS WELL AS ION-EXCHANGE RESINS, ARE marginally acceptable from an efficiency and economic standpoint, (4) OZONATION WARRANTS FURTHER LABORATORY STUDIES, BUT SHOULD NOT BE CONSIDERED FOR FIELD-SCALE STUDIES AT THIS TIME.					
DTIC QUALITY INSPECTED 3					
14. SUBJECT TERMS POWDERED CARBON/COAGULATION PROCESS, WASTEWATER, TOC, REVERSE OSMOSIS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT		

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DEPARTMENT OF THE ARMY
US ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT CENTER
FORT BELVOIR, VIRGINIA 22060

AMXFB -GS

22 December 1975

SUBJECT: Forwarding of "Treatability Studies of Seep Water
from the BOG at Rocky Mountain Arsenal"

Commander
Edgewood Arsenal
ATTN: AMCPM-DRR (Proj Mgr,
Cml Demil & Instl Restoration)
Aberdeen Proving Ground, MD
21010

FILE COPY
Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

1. Inclosed is report entitled "Treatability Studies of Seep Water from the BOG at Rocky Mountain Arsenal" dated December 1975. Subject report covers laboratory investigations of procedures, discussion of results, conclusions and recommendations for several water treatment processes utilizing carbon adsorption, reverse osmosis, and chemical oxidation for decontaminating wastewater.

2. The first phase of the study concerns the removal or destruction of trace organics in the seep water. The second phase involved selecting the most feasible processes for scale-up.

3. For any additional information relative to this report, please contact Roger Anzzolin, Autovon: 354-5696.

FOR THE COMMANDER:

1 Incl
as

RICHARD P. SCHMITT
Chief, Sanitary Sciences Division
Laboratory 2000

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Department of the Army
U.S. Army Mobility Equipment Research & Development Center
Fort Belvoir, Virginia 22060

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TREATABILITY STUDIES OF SEEP
WATER FROM THE BOG AT
ROCKY MOUNTAIN ARSENAL

R. P. CARNAHAN

D. LENT

R. ANZZOLIN

G. RUTHERFORD

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1. Summary:

a. Studies show that a powdered carbon/coagulation process is the most effective method of treating the waste water. The total organic carbon (TOC) concentration of the waste water could be reduced from 40 mg/l to 5 mg/l at a carbon dose of 2.0 grams per liter and coagulant dose of 1.0 mg/l.

b. The reverse osmosis unit reduced the TOC concentration from 40 mg/l to 8 mg/l using the PA 300 membrane. With proper design, the system should be capable of recovering 50 percent of the water.

c. Granular carbons and polymeric exchange resins are not as effective in reducing the TOC as the carbon coagulation process or the reverse osmosis process.

d. All the processes have the problem of disposal of waste streams; however, in the design of a particular process this can be minimized.

e. It is recommended that field studies be conducted at Rocky Mountain Arsenal using the carbon/coagulation process and the reverse osmosis system.

f. Additional bench-scale treatability studies need to be conducted using ozonation. The refractory compounds must be identified since they may be toxic.

*↑ means "stubborn" "obstinate"
"not yielding to treatment"*

2. Background:

a. On 12 April 1975 the Colorado State Health Department released a report on groundwater studies conducted at and around Rocky Mountain Arsenal. This report subsequently led to the issuance of a cease and desist order.

This same report charged Rocky Mountain Arsenal with allowing dicyclopentadiene and diisopropyl methyl phosphonate to contaminate groundwater. It was recommended that reclamation of the ground water begin immediately.

b. Review of the Corps of Engineers report (1961) and US Army Environmental Hygiene Agency report (1973) showed that the water table does intersect the bog in Section 24 as shown in Figure 1. Both reports contain analyses of well waters located in this section which substantiate this fact. Based upon the available information, it was concluded that, if the contaminants in the bog seep water could be removed or destroyed, then it would be feasible to attempt a reclamation program for the groundwater.

c. In June and July 1975, COL Gerald Watson, Commander RMA, Dr. William McNiell, Scientific Director RMA, and LTC Robert Carnahan, Environmental Engineer at USAMERDC, developed a plan to conduct the treatability study described in this report. These studies were started in September 1975 after receiving one hundred gallons of seep water from the bog.

3. Problem Statement: The immediate problem was to determine the applicability of unit processes, such as reverse osmosis, adsorption, and chemical oxidation, in the removal or destruction of the trace organics in the seep water. Optimizing the most feasible processes for scale-up was the second task of this study.

4. Discussion of Procedures:

a. Untreated Seep Water

(1) Upon receipt of the seep water, analyses were conducted on samples of the untreated water to determine its quality. The analyses shown in Table 1 were all conducted according to the procedures described in the

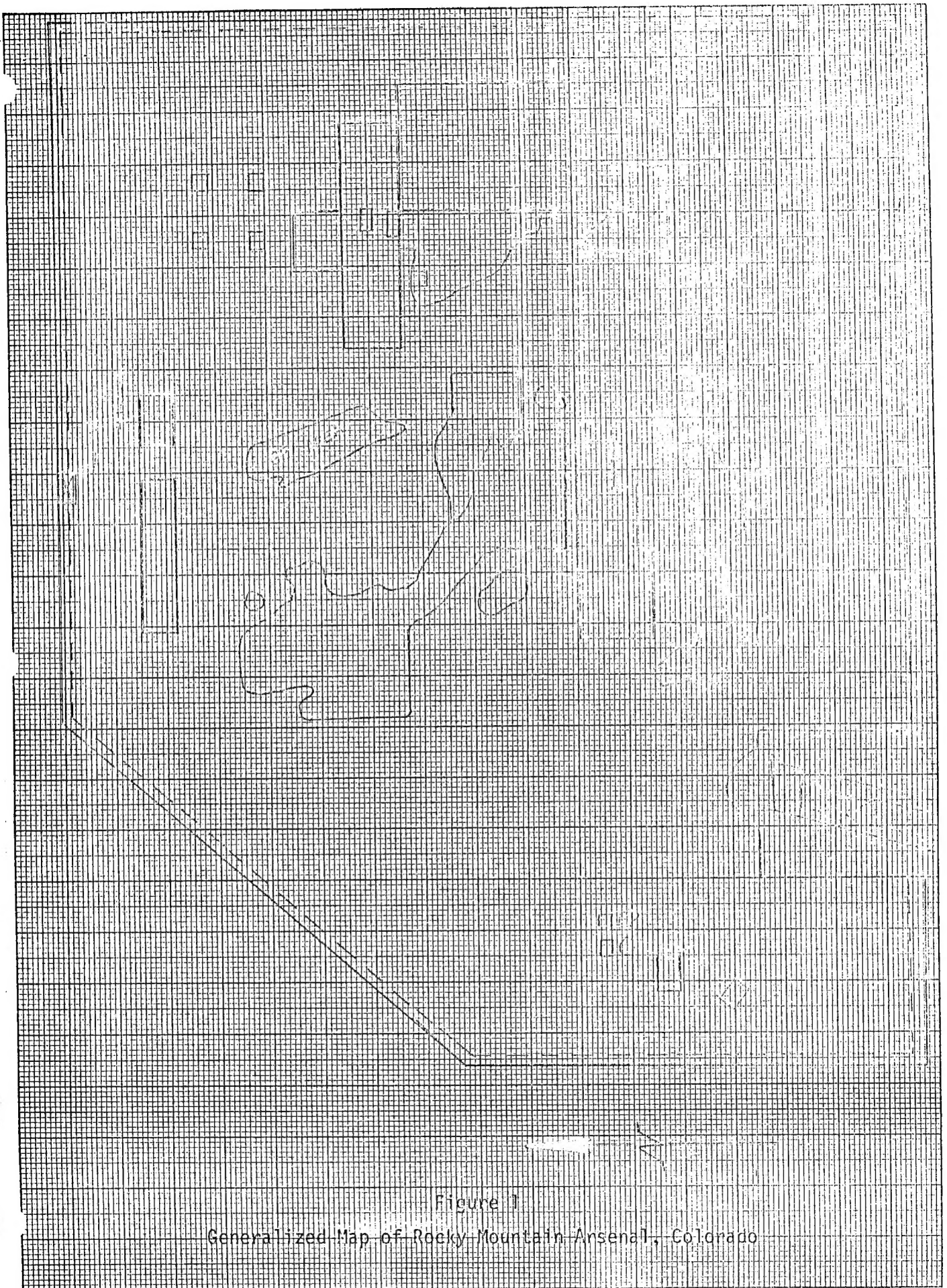


Figure 1

Generalized Map of Rocky Mountain Arsenal, Colorado

TABLE 1

ANALYSES CONDUCTED ON
UNTREATED SEEP WATER

Chemical Oxygen Demand	mg/l	COD
Total Organic Carbon	"	TOC
Total Inorganic Carbon	"	IC
Biochemical Oxygen Demand	"	BOD
Turbidity	JTU	
Color	mg/l	
pH		
Alkalinity	mg/l	ALK
Hardness	"	
Chlorides	"	Cl
Sulfates	"	SO ₄
Nitrates	"	NO ₃
Copper	"	Cu
Chromium	"	Cr
Cadmium	"	Cd
Iron	"	Fe
Conductivity	"	
Total Dissolved Solids	"	TDS

13th Edition of Standard Methods for the Examination of Water and Wastewater (1971). In addition, a wastewater sample was fingerprinted by gas chromatographic methods with a Hewlett Packard Model 7620A gas chromatograph with a 4' X 3mm ID Glass 3.8% UCW-98 on 80-100 mesh Diators S column and an electron capture detector with 63 Ni source. A Beckman Model 915 Total Carbon Analyzer was used to determine the total organic carbon (TOC) and the inorganic carbon (IC).

(2) Periodically, untreated samples were collected and analyzed to ensure the quality of the water was not changing. This also provided the base line for all treatability studies.

b. Reverse Osmosis

(1) The reverse osmosis process flow sheet is shown in Figure 2. This scheme permitted extended operating periods without changing the quality of influent water.

(2) Since the primary concern was removal of organics, a cellulose acetate and a polyamide membrane were selected for study. It was felt that this would provide a good comparison of available membranes.

(3) Based upon the total dissolved solids concentration, a pumping pressure of 400 psig and a flow rate of 4 gallons per minute were selected as operating parameters. These operating criteria proved an adequate drive force across the membranes and entrance velocity. It should be noted that, due to the difference in size of the cellulose acetate and the polyamide module, these operating conditions were not optimum for the polyamide membrane.

c. Adsorption Studies

(1) Screening studies were conducted on both granular and powdered activated carbons and both polymeric and ion exchange resins by treating

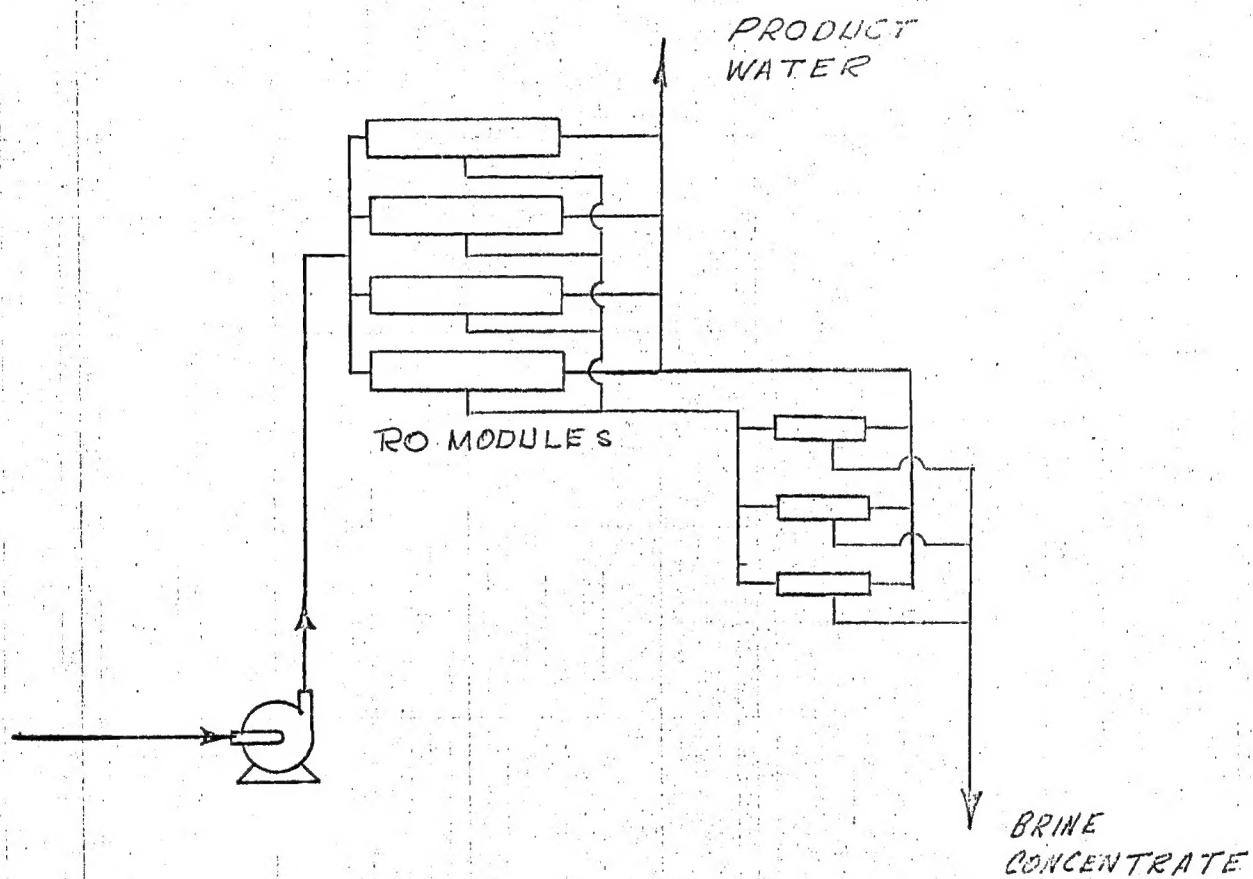


FIGURE 2 STAGE SYSTEM FOR
REVERSE OSMOSIS

liter samples of the waste with one gram of each of the adsorbents. The sample and adsorbent slurry was stirred continuously for thirty minutes and then allowed to stand for fifteen minutes to permit the separation of adsorbent from the wastewater.

(2) The treated water was then decanted and filtered. This filtered sample was then analyzed for remaining TOC concentration. Results were compared with a blank which was untreated wastewater.

(3) After selecting the most promising candidates from the screening tests, more definitive studies were conducted. In these studies, the adsorbent dosages were varied to establish optimum treating conditions. The mixing procedure, however, was the same as that previously described.

d. Ozonation Studies. These studies were conducted using an OREC Model 03C6 Ozonator which was adjusted to deliver 0.4 grams of ozone per hour. Ozone concentrations in the wastewater were determined by the method described in Standard Methods for the Examination of Water and Wastewater (1971).

5. Results:

a. Analyses of Untreated Seep Water

(1) Table 2 shows the results of analyses conducted on three samples, while Table 3 shows the results of pesticide analyses conducted by other organizations. The results obtained in Table 2 agree closely with those obtained by the US Army Environmental Hygiene Agency; Shell Chemical at Rocky Mountain Arsenal; Quality Assurance Laboratory, Rocky Mountain Arsenal; and the Colorado State Health Department.

Tables 2 & 3
are not
correlated
when are
NEHA, SCC,
RMA, and
CO State Dept.
data that agree
closely w/
Table 2.

(2) The COD and TOC analyses show reasonably good correlation as did the inorganic carbon and alkalinity analyses. These four methods were used throughout the study as checks on the laboratory analyses.

TABLE 2

RESULTS OF ANALYSES OF UNTREATED SEEP WATER

Analysis		9/12/75	9/23/75	10/24/75
Turbidity	units	3.0	1.0 unit	1.3 units
Color	units	19	18	18
Total Dissolved Solids	mg/l	1300	1350	1300
Conductivity	micromhos/cm	1850	1850	1825
pH		7.6	7.9	8.0
Alkalinity	mg/l	252	256	240
Hardness	"	488	498	466
Chlorides	"	232	239	286
Sulfates	"	627	540	620
Nitrates	"	1.5	-	-
Copper	"	0.0	0.0	
Chromium	"	0.0	0.0	
Cadmium	"	0.01	0.02	
Iron	"	0.40	0.46	
Total Organic Carbon	"	38	41	39
COD	"	31	36	40
BOD	"	<1.	<1.	

TABLE 3
PESTICIDE CONCENTRATION IN WATER

Pesticide	State Health Dept	Rocky Mt Arsenal	Shell Chemical	US Army Environmental Hygiene Agency
Aldrin	0	-	0	1.4
Dieldrin	-	-	0.6	0.5
Dicyclopenta Diene	<50	-	15	
Diisopropyl Methylphosph	0	268	340	
Endrin	1.04	-	0	2.1

Concentration in parts per billion (ppb).

(3) Based upon these results, the Total Organic Carbon (TOC) analysis was selected for use in determining the efficiency of each unit process study. The reasoning was that the pesticide concentration was much lower than the TOC concentration, which indicates that organics other than pesticides were present in the wastewater.

b. Reverse Osmosis. Figure 3 shows the results of the reverse osmosis studies using a wet cellulose acetate membrane (CA) and a polyamide membrane (PA-300). The PA-300 provided a higher flux rate and a better quality product water, while the CA membrane reduced the TOC to less than 15 mg/l. The most significant factor is the flux rate. With both membranes operating at 400 psig, the PA-300 has an average flux rate of $19.20 \pm .86$ g/sf/D while the CA membrane had an average flux of 13.45 ± 1.03 g/sf/D. *What is significant about the higher flux rate?*

c. Adsorptive Studies

(1) Table 4 shows the results obtained in screening studies using various adsorbents. Based upon these finds, extensive adsorption studies were conducted using Calgon 400, Nuchar 12X40 granular carbons, and Hydro Darco-C and Darco G-60 powdered carbons. *I think the answer is given on page 20, para 6.*

(2) Results of the Nuchar adsorption isotherm and kinetic studies are shown in Figure 4. This data indicates that a contacting time of 30 minutes would be required at an adsorption capacity of 27.4 mg/l TOC per gram of carbon. It was obvious from the preliminary data that there was leachable TOC from the carbon. After thoroughly washing and drying the carbon in distilled water, this was minimized. A question, however, does exist as to amount of leachable organic that may be expected from granular carbon.

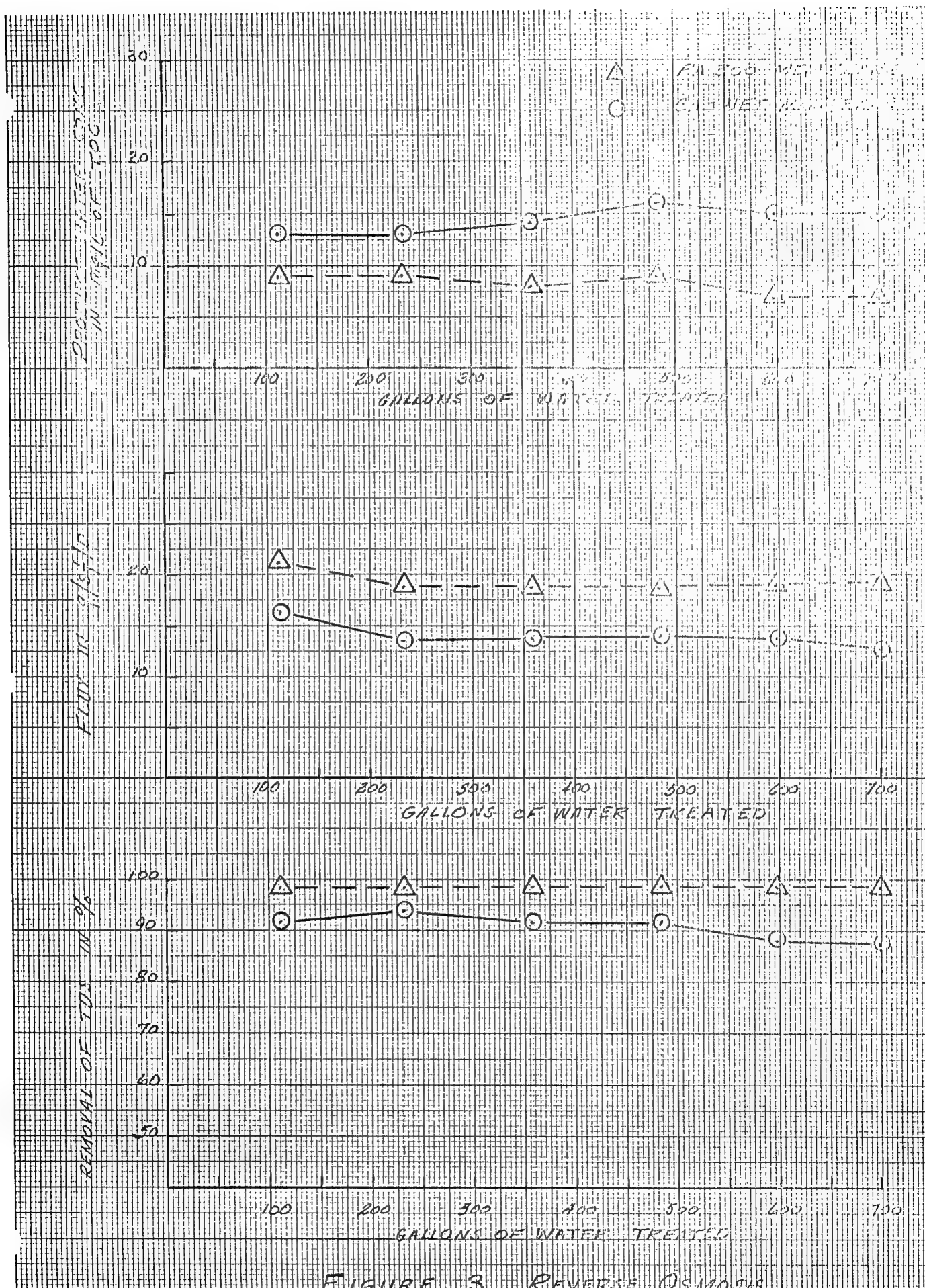


FIGURE 3 REVERSE OSMOSIS

TABLE 4		
ADSORBENT SCREENING STUDIES		
System	Adsorbent	Capacity in mg/l TOC/gm ADSORB
Granular Carbon	Calgon 400	3.99
	NUCHAR 12 X 40	10.99
Powdered Carbon	Hydro Darco-C	26.00
	Darco G-60	25.00
Resin exchangers	IRA - Anionic Resin	16.99
	NCA - Cationic Resin	7.98
	XAD-7 Poly Resin	9.01
	XAD-2 Poly Resin	7.99

EFFLUENT TOC CONC.
IN MG/L

60
50
40
30
20
10

20

40

TIME IN MINUTES

60

80

100

120

SOLID PHASE CONC. IN
MG/L

50
40
30
20
10

10

20

30

EQUILIBRIUM CONCENTRATION
IN MG/L OF TOC

40

50

60

FIGURE 4

GRANULAR

SLUDGE

(3) Adsorption isotherm for the Darco G-60 is shown in Figure 5. Regression analyses showed that the adsorption could be predicted with a correlation coefficient of 0.91 by the equation

$$X/m = 1.76 (C_{TOC}) + 5.62$$

where the C is TOC concentration remaining in milligrams per liter. The removal may be expressed by

$$\% R = 2.23 (C_{TOC}) + 97.22$$

with a correlation coefficient of 0.97 where C_{TOC} is the concentration remaining.

(4) The adsorption isotherm for the Hydro Darco-C is shown in Figure 6. Adsorption capacity using this carbon may be predicted by

$$X/m = 1.30 (C_{TOC}) + 7.60$$

with a correlation coefficient of 0.86. The efficiency of this carbon may be expressed by

$$\% R = -3.29 (C_{TOC}) + 99.49$$

with a correlation coefficient of 1.00. Based upon the limited data available, the Hydro Darco-C carbon appears to have the best adsorptive capacity for the organics in the seep water.

(5) Adsorption and coagulation studies were performed using Darco G-60 and Hydro Darco-C powdered carbon with a cationic coagulant, Catfloc, and an anionic coagulant, Drewfloc 260. The results of these studies are shown in Tables 5 and 6. The results showed that the anionic coagulant, Drewfloc 260, and Hydro Darco-C powder carbon were most effective. Figure 7 shows the optimum concentration of coagulant required.

d. Polymeric and Ionic Exchange Resins

(1) Four Amberlite resins (XAD-2, XAD-7, IRA, NCH-W) were used to

PERCENT REMOVAL OF TOC

100
90
80
70
60
50

2

4

6

8

10

12

14

16

18

20

22

24

26

28

30

EQUILIBRIUM CONC IN mg/L OF TOC

$$y = -0.002x + 0.95$$

$$r^2 = 0.97$$

SOLUBLE TOC CONC IN mg/L OF CARBON

80
70
60
50
40
30
20
10

2

4

6

8

10

12

14

16

18

20

22

24

26

28

30

EQUILIBRIUM CONCENTRATION
IN mg/L OF TOC

$$y/m = 1.176(x) + 5.62$$

$$r^2 = 0.91$$

FIGURE 5 DARCO 8-60 ADSORPTION

PERCENT DEVIATION OF \bar{M}_w

80
70
60
50
40
30
20
10

5

EQUILIBRIUM CONC IN m/l OF TOL

$\% R = 32.2$
 $r^2 = 0.99$

SOLID DYE CONC IN TOL TOLUENE
OF GREEN

20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100

5

EQUILIBRIUM CONC IN m/l OF TOL

$R_{1/2} = 1.35(0.5) = 0.675$
 $r^2 = 0.86$

FIGURE 6 HYPOTHESES

TABLE 5

Powdered Carbon with Coagulant				Cationic Polyelectrolyte*		
Catfloc Dose mg/l	DARCO G-60			HYDRO DARCO-C		
	Final TOC mg/l	Capacity mg/l TOC/ 9g ADS	% Removal	Final TOC	Capacity mg/l TOC/ 9g ADS	% Removal
5	25	3.0	10.7	21	7.0	25.0
10	16	12.0	42.9	20	8.0	28.6
20	11	17.0	60.7	24	4.0	14.3
30	15	13.0	47.4	19	9.0	32.1
40	18	10.0	35.7	19	9.0	32.1
50	11	17.0	60.7	14	14.0	50.0

*Initial conditions were - 1 gram of powder carbon per liter;
TOC concentration 28 mg/l at pH=7.4

TABLE 6
POWDERED CARBON WITH ANIONIC *
COAGULATION

Drewfloc Dose mg/l	Hydro Darco-C		
	Final TOC mg/l	Capacity mg/l TOC/gram adsorbent	% Removal
0.2	23	7.	23.
0.5	8	22.0	73.
0.5	15	15.0	50
5.0	11	19.0	63
8.0	11	19.0	63
10.0	12.5	17.5	58
10.0	19	11.0	37
15.0	28	2.0	7
20	26	4.0	13

* Initial Conditions 1 gram Carbon
Initial Concentration 30 mg/l TOC

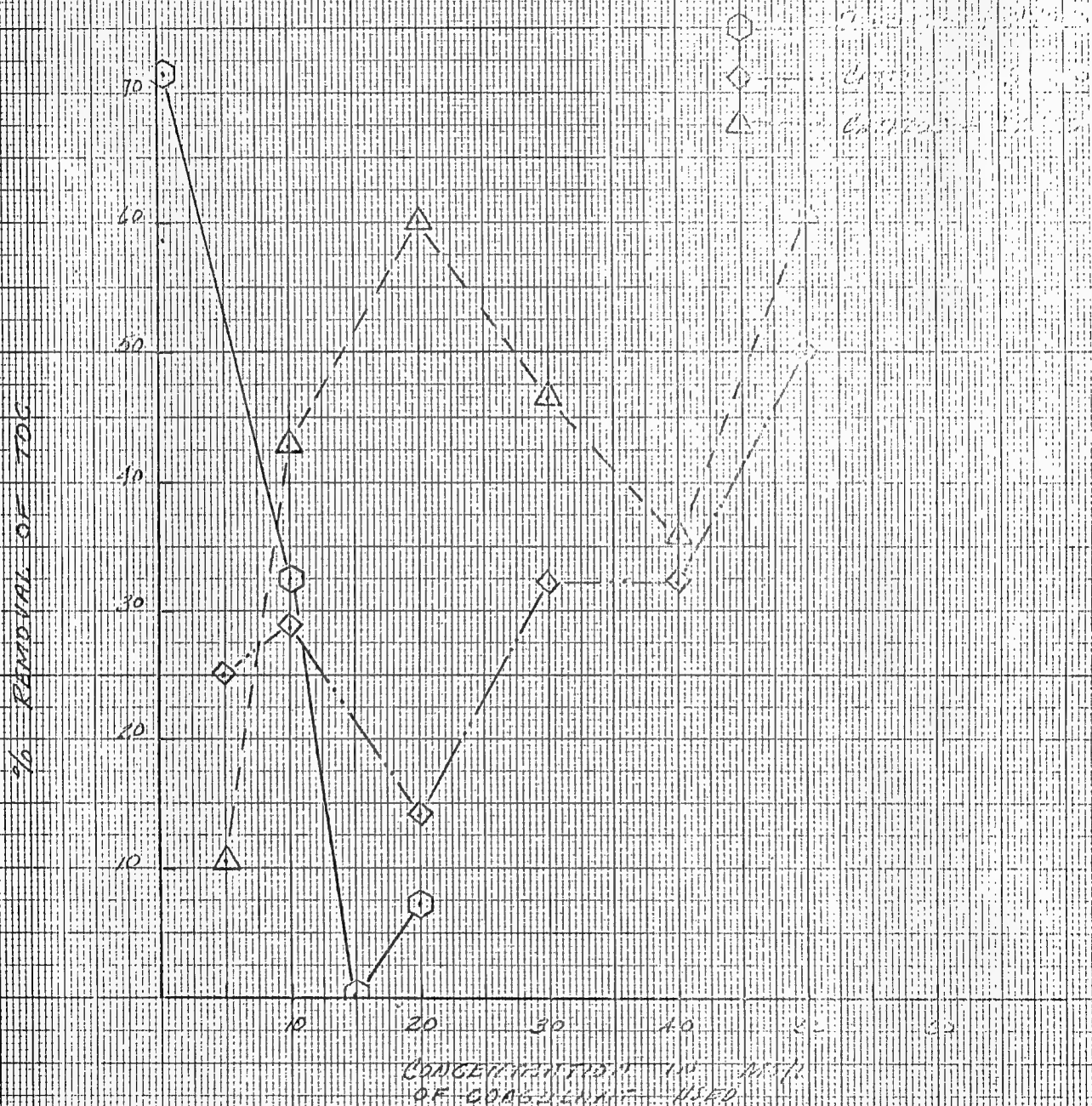


FIGURE 7. Coagulant Removal

TABLE 7 ANIONIC CAPACITY			
IRA DOSE GRAM	FINAL TOC mg/l	CAPACITY TOC mg/l GRAM RESIN	% REMOVAL
0	50	0	0
0.25	40	40	20
0.5	30	40	40
1.0	46	4	8
1.5	28	14.66	44
2.0	31	14.55	38

actual operating conditions and economic factors would have to be determined in larger scale field studies. However, from previous experiences, it is expected that the design criteria could be developed within four months after the start of these field studies.

(3) There is, however, the problem of disposing of the concentrate coming from the system, shown in Figure 2. Two alternatives exist for the disposal of the concentrate; the first is to discharge the concentrate stream into Lake F. The second alternative would be to treat the concentrate with powdered carbon and a coagulant and then recycle the water. The second alternative is the most practical economically and environmentally since the carbon/coagulation process will produce a much smaller sludge volume than the concentrate stream. This waste sludge from the carbon/coagulation process is also easily dewatered, so the volume of solids to be disposed of is much smaller than the concentrate stream.

b. Adsorption Studies

(1) The initial screening showed that granular and powdered activated carbons warranted further study. The granular carbons showed much lower capacity than expected, as shown in Table 8. The resulting effluent concentration was consistently higher than those obtained with other adsorptive processes. Neither the Calgon 400 nor Nuchar 12X40 had adequate specific sites to effectively reduce the TOC of the seep water. Due to the low capacity of these carbons, the only application of granular carbon would be as a pretreatment process.

(2) The powdered carbons exhibited high adsorptive capacity and excellent efficiency as shown by Figures 5 and 6. To effectively separate the carbon

TABLE 8 ADSORPTION ISOTHERMS FOR GRANULAR CARBON

Sample Volume (ml)	Wt of Carbon (mg)	CALGON 400		NUCHAR 12 x 40	
		Final TOC (mg)	Capacity mg/l TOC/gm ADS	Final TOC (mg)	Capacity mg/l TOC/gm ADS
1000	0	39		39	
	100	36	40	33	70
	200	36	20	33	35.5
	300	36	13.3	30	33.3
	400	36	10	29	27.5
	500	35	10	30	20.0

phase from the fluid, it was necessary to use a coagulant such as a cationic or anionic polyelectrolyte. The anionic polyelectrolyte was found to be the most effective coagulant, as indicated by Table 6. Figures 5 and 7 show that a dosage of 2 grams per liter of carbon and a coagulant dose of 1 mg/l would effectively reduce the TOC concentration from 40 mg/l to 5 mg/l. It is apparent that this process offers the greatest flexibility and control.

c. Polymeric and Ionic Exchange Resin

(1) The only resin that showed promise for treating the seep water was an intermediate-strength anionic exchange resin. This is consistent with the use of an anionic coagulant.

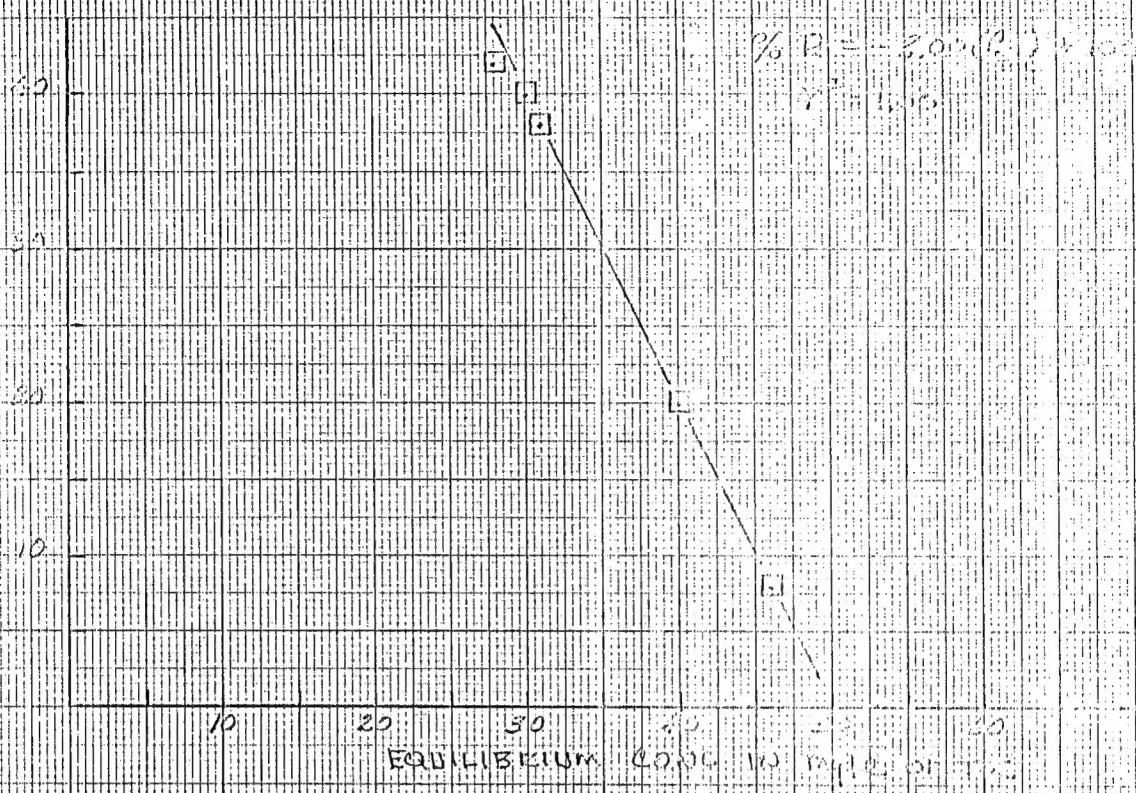
(2) Based upon the capacity curves shown in Figure 8, an ion-exchange bed of approximately 100 cf would be required to treat 125 gallons per minute. The economics of constructing such a column, plus the cost of regenerant, must be studied. The problem also arises as to disposal of the regenerant wastewater; this must also be studied.

d. Ozonation

(1) While ozonation is very effective in destroying the organic material in the seep water, additional studies are needed for the purpose of identifying the refractory residuals. The toxicity of these refractory residuals must be considered, particularly since transformations probably occur.

(2) From an economical standpoint, ozonation does not, at this time, seem feasible, since 170 grams of ozone are required to destroy one gram of TOC. The required contact time as shown in Figure 9 is one hour, which is extensive for differential contact.

PERCENT REMOVAL OF PC



SCALD DIFFER. CONC IN mg/L TOG/GR
OF
RESIN



FIGURE 8 ANIONIC RESIN

% REMAINING AS TOC

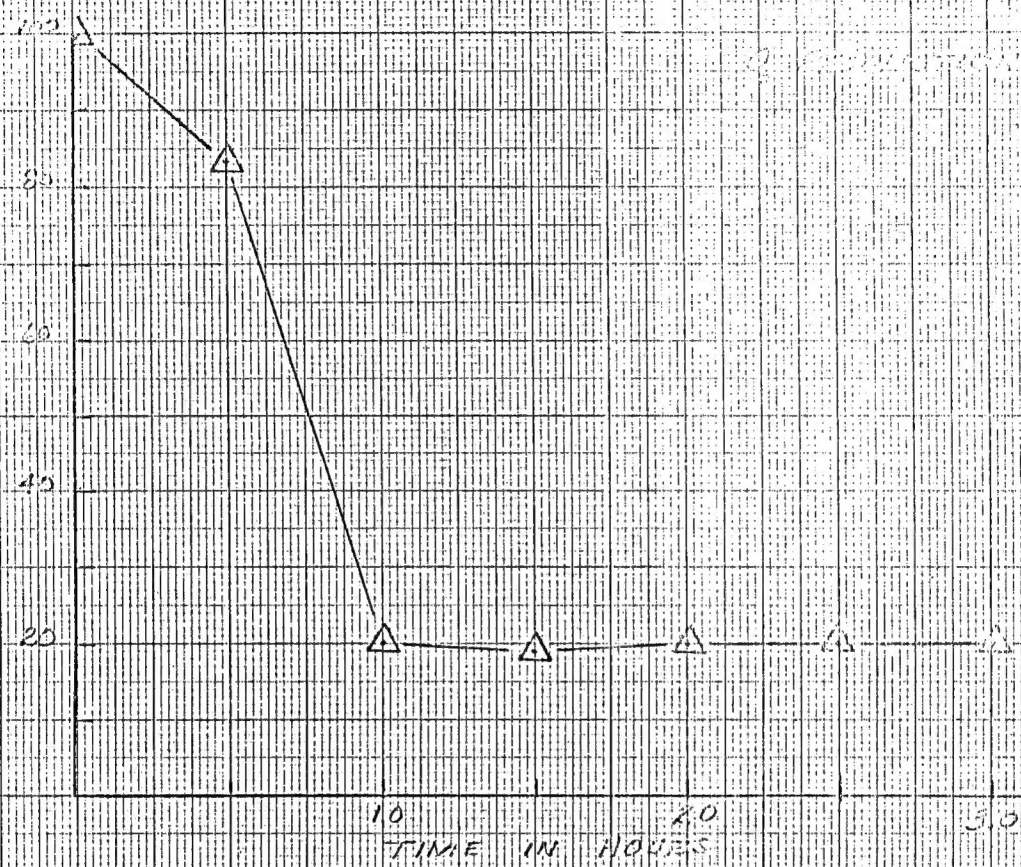


FIGURE 9 OZONATION

(3) Additional studies are being planned to determine the optimum contacting pattern and rates of reaction. Studies using UV/ozone will also be conducted to definitely establish the effectiveness of this process.

7. Conclusions:

a. The reverse osmosis process, using the PA-300 membrane, is a feasible process for treating the seep water.

b. Powder carbon/coagulation is the most practical method of treating the waste, since it provides flexibility and control within the treatment process.

c. Granular carbon adsorption, as well as ion-exchange resins, are marginally acceptable from an efficiency and economics standpoint.

d. Ozonation warrants further laboratory studies, but should not be considered for field-scale studies at this time.

8. Recommendations:

a. Field studies should be conducted at Rocky Mountain Arsenal using a 400 gallon-per-hour carbon/coagulation unit and a reverse osmosis system with PA-300 membranes.

b. Sanitary Sciences Division of the US Army Mobility Equipment Research and Development Center should provide the equipment, project engineers, and data analyses capabilities.

c. Rocky Mountain Arsenal should provide the operational staff, technical support, and laboratory analyses.